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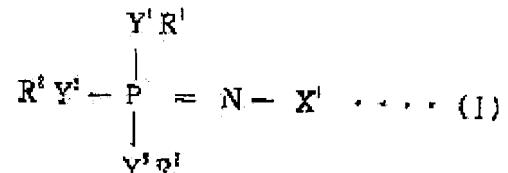
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(54) LITHIUM PRIMARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium primary cell which has a high output, a long life and a high safety because this has a high discharge capacity and a high energy density.

SOLUTION: This is the lithium primary cell provided with a positive electrode characterized that at least one kind of metal oxide selected from a group consisting of titania, alumina, zinc oxide, chromium oxide, lithium oxide, nickel oxide, copper oxide and iron oxide is dispersed among particles of manganese dioxide, a negative electrode, and an electrolytic solution composed of an aprotic organic solvent and a supporting electrolyte wherein a phosphazene derivative expressed by formula (1) and/or an isomer of the phosphazene derivative is added. In the formula, R1, R2 and R3 express a monovalent substituent or halogen element. X1 expresses a substituent including at least one kind of element selected from a group consisting of carbon, silicon, germanium, tin, nitrogen phosphorus, arsenic, antimony, bismuth, oxygen, sulfur, selenium, tellurium and polonium. Y1, Y2 and Y3 express a divalent coupling group, a divalent element or a single bond.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the lithium primary cell which is excellent in service capacity and an energy density about a lithium primary cell.

[0002]

[Description of the Prior Art] In recent years, with rapid progress of electronics, especially as a power supply of sized electronic equipment, it is small and lightweight and the cell of a long life and high energy density is called for. On the other hand, manganese dioxide is used as an anode, and since the electrode potential of lithium is the lowest in metal and the electric capacity per unit volume is large, the lithium primary cell which uses lithium as a negative electrode is known as one of the cells which has high energy density.

Many kinds of things are studied actively.

[0003] On the other hand, even if a blowout etc. arise in a pneumatic tire, the run-flat tire in which the continuous run of the considerable distance to the place which can perform repair and repair can be carried out is developed. When the internal pressure of a tire is measured and it becomes the internal pressure below fixed in connection with this, forming the internal pressure alarm equipment which transmits the signal which tells abnormalities in said run-flat tire is proposed.

[0004] Here, as a power supply of internal pressure alarm equipment, the above-mentioned small size and the lithium primary cell which is lightweight, and uses manganese dioxide of a long life and high energy density as an anode, and uses lithium as a negative electrode are used.

[0005] In a lithium primary cell, although lithium is used abundantly as a material which forms a negative electrode, in order that this lithium may react to the compound which has activity protons, such as water or alcohol, violently, the electrolyte used is restricted to a nonaqueous solution or a solid electrolyte. Since ion conductivity of a solid electrolyte is low, it is restricted only to the use in low discharge current. Therefore, the electrolysis solutions generally used now are aprotic organic solvents, such as an ester system organic solvent.

[0006]

[Problem(s) to be Solved by the Invention] However, since advanced features of internal pressure alarm

equipment were requested as transmitting the various information of a tire other than tire inner pressure and power consumption increased in connection with it, if the existing lithium primary cell was used for the power supply of internal pressure alarm equipment, the problem that it is short-life and exchange is needed for a short period of time arises.

[0007] Since negative pole materials were a lithium metal and a lithium alloy and were very high activity to moisture, obturation of the cell was imperfect, and when moisture invaded, there was a problem that it was high-risk, by a negative pole material and water reacting, and generating hydrogen or igniting, for example. Since a lithium metal was a low melting point (about 170 **), when the high current flowed rapidly at the time of a short circuit, etc., the cell generated heat unusually and it also had the problem of causing the very dangerous situation of a cell fusing. The electrolysis solution which uses an organic solvent as a base with generation of heat of the cell mentioned above evaporated and decomposed, and the problem that gas was generated or a burst and ignition of a cell took place by the emitted gas etc. also had it. Also in the lithium primary cell which originally does not assume charge, there might be charge by an operation mistake and there was also a problem of causing ignition in such a case.

[0008] Then, an object of this invention is to provide a lithium primary cell with high safety long lasting by high power, since service capacity and the energy density are high.

[0009]

[Means for Solving the Problem] In a lithium primary cell which uses manganese dioxide as an anode, this invention persons improve manganese dioxide of an anode, as a result of inquiring wholeheartedly, in order to solve said technical problem, and. By adding an isomer of a phosphazene derivative and/or a phosphazene derivative to an electrolysis solution, it finds out that a lithium primary cell long lasting with high power with high service capacity and energy density is obtained, and came to complete this invention.

[0010] Namely, a lithium primary cell this invention is characterized by that comprises the following.

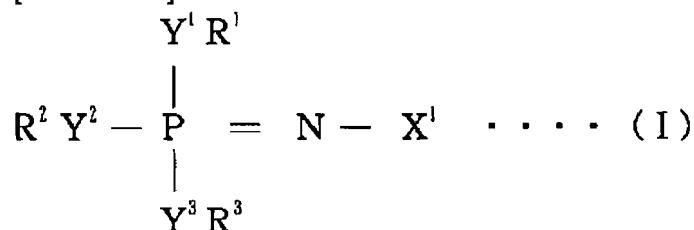
<1> Anode in which it comes to distribute at least one sort of metallic oxides chosen from a group which consists of titanium oxide, alumina, a zinc oxide, chrome oxide, lithium oxide, nickel oxide, copper oxide, and iron oxide among particles of manganese dioxide

Negative electrode.

An electrolysis solution which consists of an aprotic organic solvent in which an isomer of a phosphazene derivative and/or a phosphazene derivative was added, and a supporting electrolyte.

[0011]<2> Said phosphazene derivative is a lithium primary cell given in the above <1> characterized by what it has the viscosity below 100 mPa·s (100cP) in 25 **, and is expressed with following formula (I) or following formula (II).

[Formula 4]



(R^1 , R^2 , and R^3 express the substituent or halogen of monovalence among a formula.) X^1 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, arsenic, antimony, bismuth, oxygen, sulfur, selenium, a tellurium, and the substituent containing at least one sort of the element chosen from the group which consists of polonium. Y^1 , Y^2 , and Y^3 express a divalent connecting group, a divalent element, or a single bond.

$(NPR_2^4)_n \dots$ (II) (R^4 expresses the substituent or halogen of monovalence among a formula.) n expresses 3-15.

[0012] The phosphazene derivative expressed with <3> above-mentioned type (II) is a lithium primary cell given in the above <2> characterized by what is expressed with following formula (III).

$(NPF_2)_n \dots$ (III) (n expresses 3-13 among a formula.)

[0013] A phosphazene derivative expressed with <4> above-mentioned type (II) is a lithium primary cell given in the above <2> characterized by what is expressed with following formula (IV).

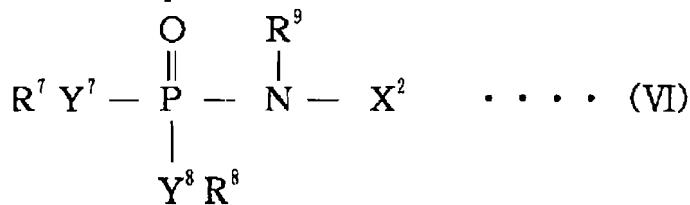
$(NPR_2^5)_n \dots$ (IV) (among a formula, R^5 expresses a substituent or fluoride of monovalence, at least one of all the R^5 is a substituent or fluoride of monovalence containing fluoride, and n expresses 3-8.) However, no R^5 is fluoride.

[0014]<5> Said phosphazene derivative is a solid in 25 **, and is a lithium primary cell given in the above <1> characterized by what is expressed with following formula (V).

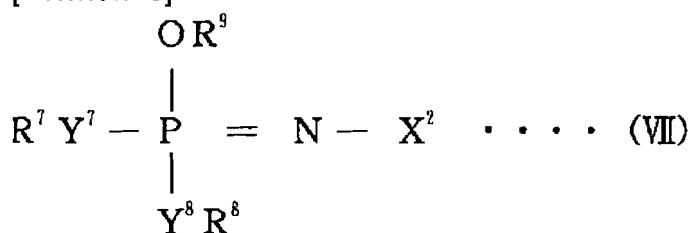
$(NPR_2^6)_n \dots$ (V) (R^6 expresses a substituent or a halogen of monovalence among a formula.) n expresses 3-6.

[0015]<6> Said isomer is a lithium primary cell given in the above <1> being an isomer of a phosphazene derivative which is expressed with following formula (VI) and expressed with following formula (VII).

[Formula 5]



[Formula 6]



(In formula (VI) and (VII), R^7 , R^8 , and R^9 express the substituent or halogen of monovalence.) X^2 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, arsenic, antimony, bismuth, oxygen, sulfur, selenium, a tellurium, and the substituent containing at least one sort of the element chosen from the group which consists

of polonium. Y⁷ and Y⁸ express a divalent connecting group, a divalent element, or a single bond.

[0016]<7> Said metallic oxide is a lithium primary cell given in any of <6> they are from the above <1> being a titanium dioxide.

<8> The mass of said metallic oxide is a lithium primary cell given in any of <7> they are from the above <1> characterized by being 0.5% to 4% to the mass of said manganese dioxide.

[0017]

[Embodiment of the Invention] Below, this invention is explained in detail. The lithium primary cell of this invention is provided with an anode, a negative electrode, and an electrolysis solution, and is provided with the member by which normal use is carried out by the technical field of lithium primary cells, such as a separator, if needed.

[0018]The anode which constitutes the lithium primary cell of this invention consists of manganese dioxide and a metallic oxide distributed among the particles of this manganese dioxide, and contains the additive agent by which normal use is carried out by the technical field of lithium primary cells, such as a conducting material and a binder, if needed.

[0019]Manganese dioxide used by this invention may be electrochemistry composition, or may be chemosynthesis. Also in the material by which normal use is carried out as an anode of a lithium primary cell, discharge potential is high capacity highly, and this manganese dioxide is excellent in safety and the wettability of an electrolysis solution, and also excellent also in respect of cost. The particle diameter of this manganese dioxide is 1-60 micrometers, and is 20-40 micrometers preferably. Since the cathode active material volume which packing worsens at the time of anode laminated wood (it consists of manganese dioxide, conducting material, and binder) shaping, or is contained in unit volume will decrease if particle diameter exceeds less than 1 micrometer or 60 micrometers, and service capacity may decrease, it is not desirable.

[0020]As a metallic oxide used for this invention, titanium oxide, alumina, a zinc oxide, chrome oxide, lithium oxide, nickel oxide, copper oxide, and iron oxide may be mentioned, and these may be independent one sort or may be two or more sorts of concomitant use.

[0021]As for this metallic oxide, it is preferred that they are very detailed particles, and the particle diameter is 10 nm - 1 micrometer, and is 20 nm - 60 nm preferably. Since the quantity of manganese dioxide as positive active material in which it is industrially contained per unit volume when particle diameter is difficult to compound and exceeds 1 micrometer decreases and the amount of energy per unit volume decreases, the particles below 10 nm are not preferred.

[0022]In this invention, since the metallic oxide is distributed among the particles of manganese dioxide, a crevice arises among manganese dioxide particles. Since an electrolysis solution can infiltrate into this crevice efficiently, the touch area of an electrolysis solution and manganese dioxide increases, the capacity factor of manganese dioxide increases as the result, and service capacity and an energy density improve. Also in the metallic oxide which forms a crevice among manganese dioxide particles, especially titanium oxide is preferred and as the reason titanium oxide, What it absorbs moisture effectively and it not only contributes to the stability of a cell, but does not reduce [not checking the cell electrode reaction of a lithium primary cell and] conductivity for remarkably by addition (internal resistance does not rise) is mentioned.

[0023]0.5 to 4% of the mass of the metallic oxide in said anode is desirable to the mass of manganese dioxide.

To the mass of manganese dioxide, if the mass of a metallic oxide is less than 0.5%, If the effect which distributes a metallic oxide among the particles of manganese dioxide, and forms a crevice is not enough and exceeds 4%, Since the particle surface of manganese dioxide is covered with a metallic oxide and the touch area of an electrolysis solution and manganese dioxide decreases, it is not desirable at the same time the amount of manganese dioxide per unit volume decreases.

[0024]As a conducting material, acetylene black etc. are mentioned to the anode which constitutes the lithium primary cell of this invention among the additive agents added if needed, and polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), etc. are mentioned to it as a binder. The blending ratio same when using these additive agents as usual, for example, the powder:conducting material for anodes,: It can blend by binder =8:1:1 - 8:1:0.2 (mass ratio).

[0025]As shape of an anode, there is no restriction in particular and it can choose suitably from shape publicly known as an electrode. For example, a sheet shaped, cylindrical shape, tabular shape, spiral shape, etc. are mentioned.

[0026]As a material of the negative electrode which constitutes the lithium primary cell of this invention, a lithium alloy besides the lithium metal itself etc. is mentioned. As metal which builds lithium and an alloy, Sn, Pb, aluminum, Au, Pt, In, Zn, Cd, Ag, Mg, etc. are mentioned. Also in these, aluminum, Zn, and Mg are preferred from the numerosness of deposits, and a toxic viewpoint. Such materials may be used by an one-sort independent, and may use two or more sorts together. As shape of a negative electrode, there is no restriction in particular and it can choose from the shape of the anode mentioned above, and the same publicly known shape suitably.

[0027]This invention is characterized by the electrolysis solution of a lithium primary cell comprising the following.

The aprotic organic solvent in which the isomer of the phosphazene derivative and/or the phosphazene derivative was added.

Supporting electrolyte.

Since the negative electrode of a lithium primary cell consists of lithium or a lithium alloy as mentioned above, its reactivity with water is dramatically high, therefore the aprotic organic solvent which does not react to a solvent with water is used for it.

[0028]As an aprotic organic solvent, although there is no restriction in particular, an ether compound, an ester compound, etc. are mentioned from a viewpoint of stopping the viscosity of an electrolysis solution low. Specifically 1,2-dimethoxyethane (DME), a tetrahydrofuran, Dimethyl carbonate, diethyl carbonate, diphenyl carbonate, ethylene carbonate, propylene carbonate (PC), gamma-butyrolactone (GBL), gamma-valerolactone, methylethyl carbonate, ethyl methyl carbonate, etc. are mentioned suitably. Chain ether compounds, such as chain ester compound [, such as cyclic ester compounds such as propylene carbonate and gamma-butyrolactone dimethyl carbonate, and methylethyl carbonate,], 1, and 2-dimethoxyethane, etc. are preferred also in these. Specific inductive capacity is preferred for especially an annular ester compound at the point of excelling in the solubility of a supporting electrolyte (lithium salt) mentioned later highly, and on the other hand, since chain ester compound and ether compound are hypoviscosity, they are preferred in respect of hypoviscosity-izing of an electrolysis solution. These may be used by an one-sort independent and may use

two or more sorts together.

[0029]What is necessary is to usually use as an ion source of a lithium ion, and as a supporting electrolyte, as an ion source of this lithium ion, [just] Although there is no restriction in particular, for example LiClO₄, LiBF₄,

LiPF₆, LiCF₃SO₃, and LiAsF₆, Lithium salt, such as LiC₄F₉SO₃, Li(CF₃SO₂)₂N, and Li(C₂F₅SO₂)₂N, is mentioned suitably. These may be used by an one-sort independent and may use two or more sorts together.

[0030]As content of the supporting electrolyte in an electrolysis solution, 0.2-1 mol is preferred to the solvent component 1L of an electrolysis solution, and 0.5-1 mol is more preferred. When content is less than 0.2 mol, while sufficient conductivity of an electrolysis solution cannot be secured but it may interfere with the discharge characteristic of a cell, in exceeding 1 mol, Since sufficient conductivity of an electrolysis solution cannot be secured like the above-mentioned since the viscosity of an electrolysis solution rises and sufficient mobility of a lithium ion cannot be secured, but solution resistance goes up as a result, it may interfere with a pulse discharge and the low-temperature characteristic.

[0031]In this invention, it is as follows as a reason for adding a phosphazene derivative to an electrolysis solution. Namely, distribute a specific metallic oxide among the particles of manganese dioxide as mentioned above, and. By adding the isomer of a phosphazene derivative and/or a phosphazene derivative to an aprotic organic solvent, the service capacity and the energy density of a lithium primary cell can be raised, and a long lasting lithium primary cell is obtained by high power.

[0032]In the electrolysis solution which used the aprotic organic solvent in a lithium primary cell as the base conventionally, When a high current flows rapidly at the time of a short circuit, etc. and a cell generates heat unusually, evaporate and decompose and gas is emitted, or, Since a burst ^{and} ignition of a cell take place with the gas and the heat which were generated, danger is high, Although the danger that the sparks produced at the time of a short circuit will ignite to an electrolysis solution, and will cause ignition and a burst is high, if the phosphazene derivative contains in the electrolysis solution of these former, Even if evaporation, disassembly, etc. of an electrolysis solution [in / comparatively / low temperature] about 200 ** or less are controlled, the danger of ignition and ignition is reduced and there is ignition inside a cell by melting of a negative pole material, etc., the danger of a spreading fire will be low. Since Lynn acts to control chain disassembly of the polymer material which constitutes a cell, the danger of said ignition ^{and} ignition is reduced effectively. If the phosphazene derivative contains in the conventional electrolysis solution, it will become possible to provide the lithium primary cell excellent also in low temperature and the elevated-temperature characteristic.

[0033]Phosphazene has only a potential window which fully functions as a primary cell, and does not decompose it by discharge. The phosphazene which the phosphazene containing halogen (for example, fluoride) functions as a scavenger of an activity radical at the time of emergency combustion, and has an organic substituent also has a screening effect of oxygen in order to generate carbide (char) on a polar material and a separator at the time of combustion. In addition, also when a user charges accidentally, since phosphazene has the depressor effect of dendrite generation, as compared with an additive-free system, safety becomes high more.

[0034]In this invention, the oxygen-index measurement according to JIS K7201 estimated the danger of ignition ^{and} ignition. In the bottom of the predetermined test condition of the regulation to JIS K 7201 with an

oxygen index, The value of the minimum oxygen density expressed with percent by volume required for material to maintain combustion is said, it means that that an oxygen index is low has the high danger of ignition and ignition, and that an oxygen index is high on the contrary means that the danger of ignition and ignition is low. This application estimated the danger of ignition and ignition with the limiting oxygen index according to the above-mentioned oxygen index.

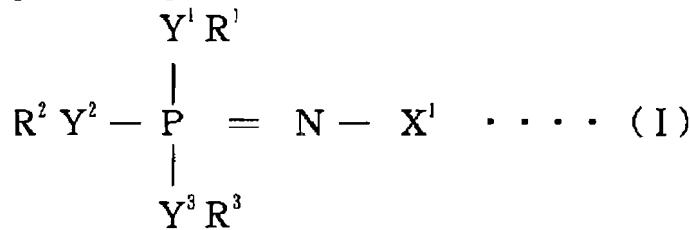
[0035]As for the electrolysis solution in which the isomer of the phosphazene derivative and/or the phosphazene derivative was added, it is preferred that a limiting oxygen index is more than 21 volume %. When a limiting oxygen index is less than 21 volume %, the depressor effect of ignition and ignition is not sometimes enough. Under an ambient condition, since an oxygen index is equivalent to 20.2 volume %, limiting-oxygen-index 20.2 volume % means burning in the atmosphere. Artificers' thing for which it has incombustibility by examination wholeheartedly if it is more than limiting-oxygen-index 21 volume %, it is more than 23 volume % about self-extinguishing and it is more than 25 volume % about fire retardancy was found out.

[0036]The self-extinguishing, fire retardancy, and incombustibility written here, Define as the method based on UL94 HB method, infiltrate the electrolysis solution of 1.0 ml into a noncombustible quartz fiber, and a specimen (127 mm x 12.7 mm) is produced, It digests, while the flame which lit is a 25-100-mm line, when this specimen is lit under atmospheric environment, And the case where ignition is not observed in the falling object from a net, either is made into those with self-extinguishing, Make the case where the flame which lit did not reach to the 25-mm line of a device, and ignition is not observed in the falling object from a net, either into fire-resistant ****, and let the case (combustion length of 0 mm) where ignition is not accepted be those with noncombustible.

[0037]As a phosphazene derivative added to an aprotic organic solvent, Although there is no restriction in particular, viscosity is comparatively low and the phosphazene derivative which the viscosity at 25 ** is below 100 mPa·s (100cP), and is expressed with following formula (I) or following formula (II) from a viewpoint of dissolving a supporting electrolyte good is preferred.

[0038]

[Formula 7]



(R^1 , R^2 , and R^3 express the substituent or halogen of monovalence among a formula.) X^1 expresses the organic group containing at least one sort of the element chosen from carbon, silicon, germanium, tin, nitrogen, Lynn, arsenic, antimony, bismuth, oxygen, sulfur, selenium, a tellurium, and the group that consists of polonium. Y^1 , Y^2 , and Y^3 express a divalent connecting group, a divalent element, or a single bond. (NPR^4_2)_n ... (II) (R^4 expresses a substituent or a halogen of monovalence among a formula.) n expresses 3-

[0039]It is required to be below 100 mPa·s (100cP) as viscosity at 25 ** of a phosphazene derivative expressed with formula (I) or formula (II), and below 20 mPa·s (20cP) is preferred. If viscosity exceeds 100 mPa·s (100cP), it will become difficult to dissolve a supporting electrolyte, wettability to a positive electrode material, a separator, etc. will fall, ion conductivity will fall remarkably according to increase of viscous resistance of an electrolysis solution, and it will become deficient in performance in use under low temperature services, such as below the freezing point, especially.

[0040]In formula (I), as R¹, R², and R³, if it is a substituent or a halogen of monovalence, there will be no restriction in particular. It is a point which an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. are mentioned, and can hypoviscosity-ize an electrolysis solution also in these as a substituent of monovalence, and an alkoxy group is preferred. On the other hand, as a halogen, fluoride, chlorine, bromine, etc. are mentioned suitably. The same kind of substituent may be sufficient as all of R¹ - R³, and a substituent of a kind from which some of them differ may be sufficient as them.

[0041]As said alkoxy group, alkoxy substitution alkoxy groups, such as a methoxy group, an ethoxy basis, a propoxy group, a butoxy group, etc. a methoxyethoxy group, a methoxyethoxy ethoxy basis, etc. are mentioned, for example. Also in these, all are preferred for a methoxy group, an ethoxy basis, a methoxyethoxy group, or a methoxyethoxy ethoxy basis as R¹ - R³, and it is preferred that a viewpoint of hypoviscosity and high permittivity to all are especially a methoxy group or an ethoxy basis.

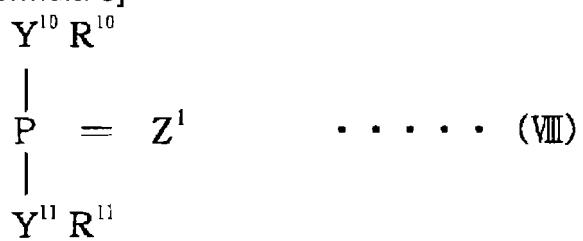
[0042]As said alkyl group, a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, etc. are mentioned. As said acyl group, a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, etc. are mentioned. As said aryl group, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As for a hydrogen element in a substituent of such monovalence, being replaced by halogen is preferred, and fluoride, chlorine, bromine, etc. are suitably mentioned as a halogen.

[0043]In formula (I), as a divalent connecting group expressed with Y¹, Y², and Y³, For example, sulfur, selenium, oxygen, nitrogen besides CH₂ group, boron, Aluminum, a scandium, gallium, yttrium, indium, A lanthan, thallium, carbon, silicon, titanium, tin, germanium, A zirconium, lead, Lynn, vanadium, arsenic, niobium, antimony, Tantalum, bismuth, chromium, molybdenum, a tellurium, polonium, tungsten, A divalent connecting group containing at least one sort of an element chosen from a group which consists of iron, cobalt, and nickel is mentioned, A divalent connecting group containing at least one sort of an element chosen from a group which consists of CH₂ group and oxygen, sulfur, selenium, and nitrogen also in these is preferred, and especially a divalent connecting group containing an element of sulfur and/or selenium is preferred. Y¹, Y², and Y³ may be divalent elements, such as oxygen, sulfur, and selenium, or a single bond. An identical kind may be sufficient as all of Y¹ - Y³, and a kind from which some differ mutually may be sufficient as them.

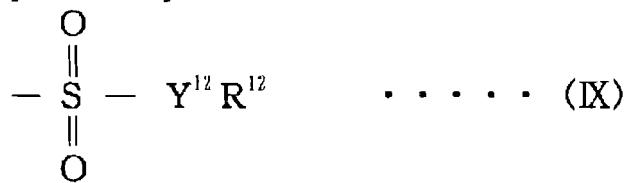
[0044]In formula (I), an organic group which contains at least one sort of carbon, silicon, nitrogen, Lynn, oxygen, and an element chosen from a group which consists of sulfur from a viewpoint of consideration of hazardous property, environment, etc. as X¹ is preferred. An organic group which has the structure expressed with following formula (VIII), (IX), or (X) among these organic groups is more preferred.

[0045]

[Formula 8]



[Formula 9]



[Formula 10]



However, in formula (VIII), (IX), and (X), $\text{R}^{10} - \text{R}^{14}$ express the substituent or halogen of monovalence. $\text{Y}^{10} - \text{Y}^{14}$ express a divalent connecting group, a divalent element, or a single bond, and Z^1 expresses a divalent basis or divalent element.

[0046] In formula (VIII), (IX), and (X), each substituents or halogens of the same monovalence are mentioned suitably as R^1 in formula (I) - R^3 described as $\text{R}^{10} - \text{R}^{14}$. A kind from which respectively same kind may be sufficient and some differ mutually in the same organic group may be sufficient as these. It may combine with each other and R^{10} and R^{11} of formula (VIII), and R^{13} and R^{14} of formula (X) may form a ring.

[0047] In formula (VIII), (IX), and (X), as a basis expressed with $\text{Y}^{10} - \text{Y}^{14}$, The same divalent connecting group or divalent element is mentioned, and similarly, when it is a basis containing an element of sulfur and/or selenium, especially in order that the danger of ignition and ignition of an electrolysis solution may decrease, it is as desirable as Y^1 in formula (I) - Y^3 described. A kind from which respectively same kind may be sufficient and some differ mutually in the same organic group may be sufficient as these.

[0048] In formula (VIII), they are CH_2 group and CHR (R expresses an alkyl group, an alkoxy group, a phenyl group, etc.) as Z^1 , for example. It is the same as that of the following. Sulfur, selenium, oxygen, boron besides a basis and NR basis, aluminum, A scandium, gallium, yttrium, indium, a lanthanum, thallium, Carbon, silicon, titanium, tin, germanium, a zirconium, lead, Lynn, Vanadium, arsenic, niobium, antimony, tantalum, bismuth, chromium, A divalent basis containing at least one sort of an element chosen from a group which consists of molybdenum, a tellurium, polonium, tungsten, iron, cobalt, and nickel are mentioned, A divalent basis containing at least one sort of an element chosen from a group which consists of oxygen, sulfur, and selenium besides CH_2 group, a CHR basis, and NR basis also in these is preferred. In the case of a divalent basis which

contains an element of sulfur and/or selenium especially, it is desirable in order that the danger of ignition and ignition of an electrolysis solution may decrease. Z^1 may be divalent elements, such as oxygen, sulfur, and selenium.

[0049]It is the point that the danger of ignition and ignition can be especially reduced effectively as these organic groups, and especially an organic group including Lynn which is expressed with formula (VIII) is preferred. Especially when an organic group is an organic group containing sulfur that it is expressed with formula (IX), it is desirable in respect of formation of small interfacial resistance of an electrolysis solution.

[0050]In formula (II), as R^4 , if it is a substituent or a halogen of monovalence, there will be no restriction in particular. It is a point which an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. are mentioned, and can hypoviscosity-ize an electrolysis solution also in these as a substituent of monovalence, and an alkoxy group is preferred. On the other hand, as a halogen, fluoride, chlorine, bromine, etc. are mentioned suitably, for example. As this alkoxy group, for example, a methoxy group, an ethoxy basis, a methoxyethoxy group, a propoxy group, a phenoxy group, etc. are mentioned, and a methoxy group, an ethoxy basis, and especially n-propoxy group are preferred also in these. As for a hydrogen element in these substituents, being replaced by halogen is preferred, and fluoride, chlorine, bromine, etc. are suitably mentioned as a halogen.

[0051] R^1 in formula (I), (II), (VIII) - (X) - R^4 , It becomes compoundable [a phosphazene derivative which has solubility suitable for more suitable viscosity, and addition and mixing etc.] by choosing suitably R^{10} - R^{14} , Y^1 - Y^3 , Y^{10} - Y^{14} , and Z^1 . These phosphazene derivative may be used by an one-sort independent, and may use two or more sorts together.

[0052]It is preferred to have a substituent which contains a halogen in molecular structure as a phosphazene derivative expressed with formula (I) or formula (II). if it has a substituent which contains a halogen in molecular structure, halogen gas derived from a phosphazene derivative will enable it more effectively to reduce the danger of ignition and ignition of an electrolysis solution also of smaller content in in a numerical value range of content of a phosphazene derivative. Although generating of halogen radicals may pose a problem in a compound which contains a halogen in a substituent, Such a problem is not generated, in order that a phosphorus element in molecular structure may catch halogen radicals and a phosphazene derivative expressed with formula (I) or formula (II) may form stable phosphorus halide.

[0053]As content in a phosphazene derivative of a halogen, 2 to 80 % of the weight is preferred, 2 to 60 % of the weight is more preferred, and 2 to 50 % of the weight is still more preferred. Since viscosity will become high if it exceeds 80 % of the weight while an effect in which content includes a halogen in less than 2 % of the weight may not fully show up, when it adds to an electrolysis solution, the conductivity may fall. Especially as a halogen, fluoride, chlorine, bromine, etc. are preferred and a viewpoint of obtaining a good battery characteristic also in this to especially fluoride is preferred.

[0054]As content of a phosphazene derivative expressed with formula (I) or formula (II) to an electrolysis solution, from a viewpoint of a limiting oxygen index, more than 5 volume % is preferred, and 10 to 50 volume % is more preferred. By adjusting content to a value in said numerical value range, the danger of ignition and ignition of an electrolysis solution is reduced effectively. Although the danger of ignition is reduced effectively,

the range is optimized by texture ***** timely in content which it changes with a kind of supporting electrolyte to be used, or kinds of electrolysis solution, and a specifically used system is most stopped by hypoviscosity, and a limiting oxygen index becomes more than 21 volume %.

[0055]Especially a phosphazene derivative expressed with following formula (III) from a viewpoint [hypoviscosity-izes an electrolysis solution, and raise the low-temperature characteristic of a cell, and also] of raising degradation-proof nature and safety of an electrolysis solution also in a phosphazene derivative of said formula (II) is preferred.

(NPF₂)_n ... (III) (n expresses 3-13 among a formula.)

[0056]As a desirable reason, a phosphazene derivative expressed with the above-mentioned formula (III) is as follows. Namely, in an electrolysis solution containing a supporting electrolyte used as an ester system organic solvent used for the conventional lithium primary cell, and a source of a lithium ion, A supporting electrolyte decomposes with temporality, when a decomposition product reacts to a little water etc. which exist in an organic solvent, the conductivity of an electrolysis solution may fall or degradation of a polar material may be produced. On the other hand, if a phosphazene derivative expressed with formula (III) by the conventional electrolysis solution is added, decomposition of a supporting electrolyte will be controlled and the stability of an electrolysis solution will improve remarkably. Generally as a supporting electrolyte, LiBF₄, LiPF₆, LiCF₃SO₃, Li(C₂F₅SO₂)₂N, LiCF₃SO₃ with low hydrolysis of the supporting electrolyte itself in which Li(CF₃SO₂)₂N etc. are used, Although Li(C₂F₅SO₂)₂N and especially Li(CF₃SO₂)₂N are preferred, LiBF₄ and LiPF₆ can also be conveniently used by the above-mentioned operation of phosphazene.

[0057]A phosphazene derivative expressed with formula (III) is a fluid of hypoviscosity at ordinary temperature (25 **), and has a depression-of-freezing-point operation. For this reason, it becomes possible to give the low-temperature characteristic which was excellent in an electrolysis solution by adding this phosphazene derivative to an electrolysis solution, and hypoviscosity-ization of an electrolysis solution is attained and it becomes possible to provide a lithium primary cell which has low internal resistance and high conductivity. For this reason, in low rural areas and a stage of especially atmospheric temperature, even if it uses it under a low temperature service, it becomes possible to provide a lithium primary cell in which a discharge characteristic outstanding over a long time is shown.

[0058]In formula (III), as n, the low-temperature characteristic excellent in an electrolysis solution can be given, and it is a point in which hypoviscosity-izing of an electrolysis solution is possible, and 3-4 are preferred and 3 is more preferred. When a value of n is small, the boiling point can be low and can raise the ignition prevention characteristic at the time of an approaching flame. On the other hand, since the boiling point becomes high as a value of n becomes large, it can be stably used also at an elevated temperature. In order to obtain the target performance using the above-mentioned character, it is also possible to choose two or more phosphazene timely and to use it.

[0059]By choosing an n value in formula (III) suitably, preparation of an electrolysis solution which has more suitable viscosity, solubility suitable for mixing, the low-temperature characteristic, etc. is attained. These phosphazene derivatives may be used by an one-sort independent, and may use two or more sorts together.

[0060]As viscosity of a phosphazene derivative expressed with formula (III), 20 If it is below mPa·s (20 cP), there

will be no restriction in particular, but from a viewpoint of conductive improvement and improvement in the low-temperature characteristic, below 10 mPa·s (10 cP) is preferred, and below 5 mPa·s (5 cP) is more preferred. in addition -- in this invention -- viscosity -- a measurement-of-viscosity meter (R form viscosity meter Model RE500-SL.) Using a product made from East Opportunity Industry, 1 rpm, 2 rpm, 3 rpm, 5 It measured for 120 seconds at a time with each revolving speed of rpm, 7 rpm, 10 rpm, 20 rpm, and 50 rpm, revolving speed when indicated value became 50 to 60% was made into an analysis condition, and it asked by measuring viscosity in that case.

[0061]Since a phosphazene derivative expressed with formula (III) does not have the flash point, it becomes possible to reduce a danger of ignition etc. being controlled, and an electrolysis solution containing this phosphazene derivative igniting even if ignition etc. arise inside a cell, and spreading to the electrolysis solution surface.

[0062]As a total content of a phosphazene derivative expressed with formula (III) in an electrolysis solution, By an effect acquired by containing this phosphazene derivative. Four kinds of content, the 1st content that can give the "low-temperature characteristic" suitably for an electrolysis solution, the 2nd content that can give "degradation-proof nature" suitably for an electrolysis solution, the 3rd content that can carry out "hypoviscosity-ization" of the electrolysis solution suitably, and the 4th content that can give "safety" suitably with an electrolysis solution, are mentioned.

[0063]More than 1 volume % of the 1st content of a phosphazene derivative expressed with formula (III) in an electrolysis solution from a viewpoint of the "low-temperature characteristic" is preferred, more than its 3 volume % is more preferred, and more than its 5 volume % is still more preferred. Unless content is less than 1 volume %, a coagulating point of an electrolysis solution cannot be made low enough, and the low-temperature characteristic is not enough.

[0064]More than 2 volume % of the 2nd content of a phosphazene derivative expressed with formula (III) in an electrolysis solution from a viewpoint of "degradation-proof nature" is preferred, and its 3 - 75 volume % is more preferred. From a viewpoint that it is highly compatible in the low-temperature characteristic and degradation-proof nature, 5 - 75 volume % is more preferred. If content is in said numerical value range, it can control degradation suitably.

[0065]More than 3 volume % of the 3rd content of a phosphazene derivative expressed with formula (III) in an electrolysis solution from a viewpoint of "hypoviscosity-izing" is preferred, its 3 - 80 volume % is more preferred, and less than its 3 - 50 volume % is still more preferred. From a viewpoint that it is highly compatible in the low-temperature characteristic, degradation-proof nature, and hypoviscosity-ization, 5 - 80 volume % is preferred, and less than 3 - 50 volume % is more preferred. Content cannot fully carry out [hypoviscosity]-izing of the electrolysis solution in less than 3 volume %. Since viscosity of propylene carbonate generally widely used for an electrolysis solution is 2.5 mPa·s (2.5 cP) and phosphazene of n= 3 of this application is 0.8 mPa·s (0.8 cP), Since viscosity becomes low so that an addition of phosphazene increases, from a viewpoint of conductive improvement and improvement in the low-temperature characteristic, it is desirable, but it is not desirable in order to cause a viscosity rise of an electrolysis solution, since supporting electrolyte solubility will be saturated, if a phosphazene addition becomes more than 50 volume %.

[0066]More than 5 volume % of the 4th content of a phosphazene derivative expressed with formula (III) in an

electrolysis solution from a viewpoint of "safety" is preferred. Since safety becomes high and a limiting oxygen index of an electrolysis solution becomes by adjusting this content more than 5 volume % more than 21 volume % so that there is much content of phosphazene, the danger of ignition and ignition is reduced effectively. The above-mentioned oxygen-index measurement can estimate safety.

[0067]Especially a phosphazene derivative expressed with following formula (IV) from a viewpoint of raising degradation-proof nature and safety of an electrolysis solution, also in a phosphazene derivative of said formula (II) is preferred.

$(NPR_2^5)_n \dots$ (IV) (among a formula, R^5 expresses a substituent or fluoride of monovalence, at least one of all the R^5 is a substituent or fluoride of monovalence containing fluoride, and n expresses 3-8.) However, no R^5 is fluoride.

[0068]As a desirable reason, a phosphazene derivative expressed with the above-mentioned formula (IV) is as follows. Namely, if a phosphazene derivative is contained, can give self-extinguishing thru/or fire retardancy excellent in an electrolysis solution, and can raise the safety of an electrolysis solution, but. It is expressed with formula (IV), and if at least one of all the R^5 contains a phosphazene derivative which is a substituent of monovalence containing fluoride, it will become possible to give safety outstanding with an electrolysis solution. If it is expressed with formula (IV) and at least one of all the R^5 contains a phosphazene derivative which is fluoride, it will become possible to give further outstanding safety. Namely, it is expressed with formula (IV) compared with a phosphazene derivative which does not contain fluoride, A phosphazene derivative which is a substituent or fluoride of monovalence in which at least one of all the R^5 contains fluoride has an effect which make it harder to burn in an electrolysis solution, and can give safety further outstanding to an electrolysis solution.

[0069]The annular phosphazene derivative itself in which all the R^5 is fluoride in formula (IV) and whose n is 3 is incombustibility, Although an effect of preventing ignition at the time of flame approaching is large, since the boiling point is dramatically low, an aprotic organic solvent etc. which were left behind after they all volatilized will burn.

[0070]It is the point of an alkyl group, an acyl group, an aryl group, a carboxyl group, etc. besides an alkoxy group being mentioned, and excelling especially in improvement in the safety of an electrolysis solution as a substituent of monovalence in formula (IV), and an alkoxy group is preferred. It is the point of alkoxy group substitution alkoxy groups etc. which are a methoxy group, an ethoxy basis, n-propoxy group, i-propoxy group, a butoxy group, etc., such as an others and methoxyethoxy group, being mentioned as an alkoxy group, and excelling in improvement in the safety of an electrolysis solution, A methoxy group, an ethoxy basis, and especially n-propoxy group are preferred. In respect of hypoviscosity-izing of an electrolysis solution, a methoxy group is preferred. In formula (IV), it is a point which can give safety excellent in an electrolysis solution as n, and 3-4 are preferred. When being replaced by fluoride is preferred as for a substituent of said monovalence and one R^5 of formula (IV) is not fluoride, either, a substituent of at least one monovalence is fluoride ****.

[0071]As content in a phosphazene derivative of said fluoride, 3 to 70 % of the weight is preferred, and 7 to 45

% of the weight is more preferred. If content is in said numerical value range, it can do so especially suitably "outstanding safety" which is a characteristic effect of this invention.

[0072]As molecular structure of a phosphazene derivative expressed with formula (IV), halogens, such as chlorine and bromine, may be included besides the above-mentioned fluoride.

[0073]By choosing suitably R⁵ and an n value in formula (IV), preparation of an electrolysis solution which has solubility suitable for more suitable safety, viscosity, and mixing etc. is attained. These phosphazene derivatives may be used by an one-sort independent, and may use two or more sorts together.

[0074]As viscosity of a phosphazene derivative expressed with formula (IV), if it is below 20 mPa·s (20 cP), there will be no restriction in particular, but from a viewpoint of conductive improvement and improvement in the low-temperature characteristic, below 10 mPa·s (10 cP) is preferred, and below 5 mPa·s (5 cP) is more preferred.

[0075]As the flash point of a phosphazene derivative expressed with formula (IV), although there is no restriction in particular, from points, such as control of ignition, not less than 100 ** is preferred, not less than 150 ** is more preferred, and not less than 300 ** is still more preferred. Here, specifically flame spreads in material surfaces, the flash point says wrap temperature for 75 % of these material surfaces at least, and this flash point serves as a measure which looks at the degree of tendency which forms air and an inflammable mixture. If a phosphazene derivative has the flash point at not less than 100 **, even if ignition etc. are controlled and ignition etc. arise inside a cell, it will become possible to reduce a danger of igniting and spreading to the electrolysis solution surface.

[0076]As a total content of a phosphazene derivative which is formula (IV) in an electrolysis solution and is expressed, Two kinds of content, the 1st content that can give "degradation-proof nature" suitably for an electrolysis solution, and the 2nd content that can give "safety" excellent in especially an electrolysis solution, are mentioned by effect acquired by containing this phosphazene derivative.

[0077]More than 2 volume % of the 1st content of a phosphazene derivative expressed with formula (IV) in an electrolysis solution from a viewpoint which can give "degradation-proof nature" suitably is preferred, and its 2 - 75 volume % is more preferred. If content is in said numerical value range, it can control degradation suitably.

[0078]More than 10 volume % of the 2nd content of a phosphazene derivative that is formula (IV) in an electrolysis solution and is expressed from a viewpoint [give "safety" more suitably and] of obtaining a very high lithium primary cell of safety is preferred, and more than its 15 volume % is more preferred. Content may be unable to give "safety" excellent in an electrolysis solution in particular by less than 10 volume %.

[0079]From a viewpoint that it is highly compatible in safety and degradation-proof nature, 10 - 75 volume % is more preferred, and 15 - 75 volume % is still more preferred. Since solubility of a supporting electrolyte will approach saturation and viscosity of an electrolysis solution will rise if a phosphazene addition becomes more than 50 volume %, in order to avoid a viscosity rise of an electrolysis solution, less than 50 volume % is preferred.

[0080]An annular phosphazene derivative expressed with formula (IV) as an electrolysis solution from a viewpoint of "safety", When LiBF₄, gamma-butyrolactone, and/or propylene carbonate are included, especially a case where an annular phosphazene derivative and LiCF₃SO₃ which are expressed with formula (IV), gamma-butyrolactone, and/or propylene carbonate are included is preferred. Safety is dramatically high, even

if it is not concerned with the above-mentioned statement in these cases but content is little. That is, in order to make outstanding safety reveal especially as content in an electrolysis solution of an annular phosphazene derivative expressed with formula (IV), more than 5 volume % is preferred. It is suitable also when aiming at using it at an elevated temperature, and $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ are included as a supporting electrolyte.

[0081]As a phosphazene derivative added to an aprotic organic solvent, A phosphazene derivative which is a solid in 25 ** (ordinary temperature), and is expressed with following formula (V) from a viewpoint [raise the degradation-proof nature of an electrolysis solution and] of giving autolysis nature thru/or fire retardancy to an electrolysis solution is also preferred, controlling a viscosity rise of an electrolysis solution.

$(\text{NPR}_2^6)_n \dots (\text{V})$ (R^6 expresses a substituent or a halogen of monovalence among a formula.) n expresses 3-6.

[0082]As an especially desirable reason, a phosphazene derivative expressed with the above-mentioned formula (V) is as follows. Namely, in an electrolysis solution containing a supporting electrolyte used as an ester system organic solvent used for the conventional lithium primary cell, and a source of a lithium ion, Although the conductivity of an electrolysis solution may fall when a supporting electrolyte decomposes with temporality and a decomposition product reacts to a little water etc. which exist in an organic solvent, or degradation of a polar material may be produced, If a phosphazene derivative expressed with formula (V) by the conventional electrolysis solution is added, decomposition of a supporting electrolyte will be controlled and stabilization of an electrolysis solution will improve remarkably. Generally as a supporting electrolyte, LiBF_4 ,

LiPF_6 , LiCF_3SO_3 , $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, LiCF_3SO_3 with low hydrolysis of the supporting electrolyte itself in which $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ etc. are used, Although $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ and especially $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ are preferred, LiBF_4 and LiPF_6 can also be conveniently used by the above-mentioned operation of phosphazene expressed with formula (V).

[0083]Since a phosphazene derivative expressed with formula (V) is a solid at ordinary temperature (25 **), if it adds to an electrolysis solution, it will dissolve in an electrolysis solution and viscosity of an electrolysis solution will rise. However, if it is a predetermined addition as mentioned later, a viscosity increasing rate of an electrolysis solution is low, and it becomes a lithium primary cell which has low internal resistance and high conductivity. In addition, since a phosphazene derivative expressed with formula (V) dissolves in an electrolysis solution, it is excellent in the long-term stability of an electrolysis solution. Internal resistance is high, and conductivity becomes low and it becomes impossible for viscosity of an electrolysis solution to become remarkably large on the other hand, if it adds exceeding a predetermined addition, and to use it as a lithium primary cell.

[0084]In formula (V), as R^6 , if it is a substituent or a halogen of monovalence, there will be no restriction in particular and an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. will be mentioned as a substituent of monovalence. As a halogen, halogens, such as fluoride, chlorine, bromine, and iodine, are mentioned suitably, for example. An alkoxy group is preferred at a point which can control especially a viscosity rise of an electrolysis solution also in these. As this alkoxy group, a methoxy group, an

ethoxy basis, a methoxyethoxy group, At a point which is preferred as for a propoxy group (an isopropoxy group, n-propoxy group), a phenoxy group, a trifluoroethoxy group, etc., and can control a viscosity rise of an electrolysis solution. A methoxy group, an ethoxy basis, a propoxy group (an isopropoxy group, n-propoxy group), a phenoxy group, a trifluoroethoxy group, etc. are more preferred. As for a substituent of said monovalence, it is preferred that the above-mentioned halogen is included. In formula (V), as n, it is a point which can control a viscosity rise of an electrolysis solution, and 3 or especially 4 is preferred.

[0085]As a phosphazene derivative expressed with formula (V), For example, structure where R⁶ is a methoxy group in said formula (V), and n is 3, Structure where a methoxy group and a phenoxy group are [R⁶] in any at least in formula (V), and n is 4, Structure where R⁶ is an ethoxy basis in formula (V), and n is 4, Structure where R⁶ is an isopropoxy group in formula (V), and n is 3 or 4, Structure where R⁶ is n-propoxy group in formula (V), and n is 4, Structure where R⁶ is a trifluoroethoxy group in formula (V), and n is 3 or 4, and structure where R⁶ is a phenoxy group in formula (V), and n is 3 or 4 are the points which can control a viscosity rise of an electrolysis solution, and are especially preferred.

[0086]By choosing suitably each substituent and an n value in formula (V), preparation of an electrolysis solution which has solubility suitable for more suitable viscosity and mixing etc. is attained. These phosphazene derivatives may be used by an one-sort independent, and may use two or more sorts together.

[0087]It is preferred to have a substituent which contains a halogen as mentioned above as molecular structure of a phosphazene derivative expressed with formula (V). As this halogen, fluoride, chlorine, bromine, etc. are preferred and especially fluoride is preferred. If it has a substituent which contains a halogen or a halogen in molecular structure, it will become possible to make self-extinguishing thru/or fire retardancy reveal at least more effectively of content of a phosphazene derivative with halogen gas derived from a phosphazene derivative. In a compound which has a substituent containing a halogen, although generating of halogen radicals may pose a problem, Such a problem is not generated, in order that a phosphorus element in molecular structure may catch halogen radicals and a phosphazene derivative used by this invention may form stable phosphorus halide.

[0088]As halogen content of the phosphazene derivation inside of the body of formula (V) containing a halogen content substituent, 2 to 80 % of the weight is preferred, 2 to 60 % of the weight is more preferred, and 2 to 50 % of the weight is still more preferred. If it exceeds 80 % of the weight while an effect that content makes a halogen contain in less than 2 % of the weight may not fully show up, when it adds to an electrolysis solution, viscosity will rise, and conductivity will fall.

[0089]As the flash point of a phosphazene derivative expressed with formula (V), although there is no restriction in particular, from points, such as control of ignition, not less than 100 ** is preferred, and not less than 150 ** is more preferred. If a phosphazene derivative has the flash point at not less than 100 **, even if ignition etc. are controlled and ignition etc. arise inside a cell, it will become possible to reduce a danger of igniting and spreading to the electrolysis solution surface.

[0090]As content of a phosphazene derivative expressed with formula (V) in an electrolysis solution, By an effect acquired by containing this phosphazene derivative. Four kinds of content of the 2nd content which "viscosity rise control" of an electrolysis solution can give "degradation-proof nature" suitably for the 1st

possible content and an electrolysis solution, the 3rd content that can give "self-extinguishing" suitably for an electrolysis solution, and the 4th content that can give "fire retardancy" suitably for an electrolysis solution are mentioned.

[0091]As for the 1st content of a phosphazene derivative expressed with formula (V) in an electrolysis solution from a viewpoint of "viscosity rise control", 40 or less % of the weight is preferred, its 35 or less % of the weight is more preferred, and its 30 or less % of the weight is still more preferred. If content exceeds 40 % of the weight, a viscosity rise of an electrolysis solution becomes remarkably large, internal resistance is high, and conductivity becomes low and is not preferred.

[0092]As for the 2nd content of a phosphazene derivative expressed with formula (V) in an electrolysis solution from a viewpoint of "degradation-proof nature", 2 % of the weight or more is preferred. If content is in said numerical value range, it can control degradation suitably.

[0093]From a viewpoint of "self-extinguishing", the 3rd content of a phosphazene derivative expressed with formula (V) in an electrolysis solution, 20 % of the weight or more is preferred, from a viewpoint that it is highly compatible in self-extinguishing and control of a viscosity rise, 20 to 40 % of the weight is more preferred, 20 to 35 % of the weight is still more preferred, and especially 20 to 30 % of the weight is preferred. Content cannot make sufficient self-extinguishing for an electrolysis solution reveal in less than 20 % of the weight.

[0094]As for the 4th content of a phosphazene derivative expressed with formula (V) in an electrolysis solution from a "fire-resistant" viewpoint, 30 % of the weight or more is preferred, from a viewpoint that it is highly compatible in fire retardancy and control of a viscosity rise, 30 to 40 % of the weight is more preferred, and 30 to 35 % of the weight is still more preferred. If content is 30 % of the weight or more, it will become possible to make sufficient fire retardancy for an electrolysis solution reveal of it. The above-mentioned oxygen-index measurement can estimate the self-extinguishing of an electrolysis solution thru/or fire retardancy.

[0095]From a viewpoint of "self-extinguishing thru/or fire retardancy", as an electrolysis solution, When a phosphazene derivative and LiBF₄ which are expressed with formula (V), gamma-butyrolactone, and/or propylene carbonate are included, And especially a case where a phosphazene derivative and LiCF₃SO₃ which are expressed with formula (V), gamma-butyrolactone, and/or propylene carbonate are included is preferred. It is not concerned with the above-mentioned statement in these cases, but even if said content is little, it has outstanding self-extinguishing thru/or a fire-resistant effect.

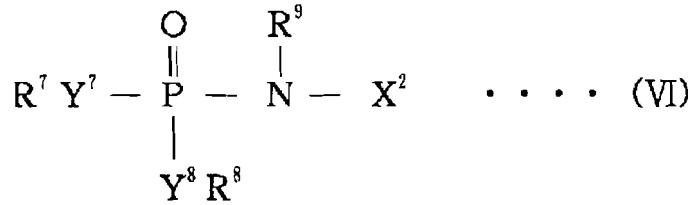
[0096]Namely, a phosphazene derivative, LiBF₄ which are expressed with formula (V), When gamma-butyrolactone and/or propylene carbonate are included, as content in an electrolysis solution of this phosphazene derivative, In order 5 to 10 % of the weight is preferred in order to make self-extinguishing reveal, and to make fire retardancy reveal, Quantity exceeding 10 % of the weight is preferred, 40 or less % of the weight is more preferred, and it exceeds 10 % of the weight, and 35 or less % of the weight is still more preferred, it exceeds [from a viewpoint that it is highly compatible in fire retardancy and control of a viscosity rise, it exceeds 10 % of the weight, and] 10 % of the weight, and especially 30 or less % of the weight is preferred.

[0097]A phosphazene derivative, LiCF₃SO₃ which are expressed with formula (V), When gamma-butyrolactone and/or propylene carbonate are included, as content in an electrolysis solution of this

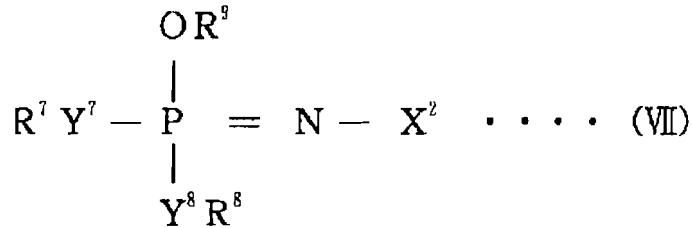
phosphazene derivative, In order 5 to 25 % of the weight is preferred in order to make self-extinguishing reveal, and to make fire retardancy reveal, Quantity exceeding 25 % of the weight is preferred, 40 or less % of the weight is more preferred, and it exceeds 25 % of the weight, and 35 or less % of the weight is still more preferred, it exceeds [from a viewpoint that it is highly compatible in fire retardancy and control of a viscosity rise, it exceeds 25 % of the weight, and] 25 % of the weight, and especially 30 or less % of the weight is preferred.

[0098]As an isomer of a phosphazene derivative added to an aprotic organic solvent, Although not restricted in particular, the low-temperature characteristic of a lithium primary cell is raised, autolysis nature thru/or fire retardancy are given to an electrolysis solution, and an isomer of a phosphazene derivative which is expressed with following formula (VI) and expressed with following formula (VII) from a viewpoint of raising the degradation-proof nature of an electrolysis solution is still more preferred.

[Formula 11]



[Formula 12]



(In formula (VI) and (VII), R^7 , R^8 , and R^9 express the substituent or halogen of monovalence.) X^2 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, arsenic, antimony, bismuth, oxygen, sulfur, selenium, a tellurium, and the substituent containing at least one sort of the element chosen from the group which consists of polonium. Y^7 and Y^8 express a divalent connecting group, a divalent element, or a single bond.

[0099]An isomer of a phosphazene derivative which is expressed with formula (VI) and expressed with formula (VII) is as follows as a desirable reason. Namely, an isomer of a phosphazene derivative which is expressed with formula (VI) and expressed with formula (VII) has only a potential window which fully functions as a primary cell, and does not decompose it by discharge. Since self-extinguishing thru/or fire retardancy which was excellent in an electrolysis solution by operation of nitrogen gas, halogen gas, etc. which are derived from this isomer is given, as for a lithium primary cell having contained this electrolysis solution, safety becomes high. An isomer of a phosphazene derivative which is expressed with formula (VI) and expressed with formula (VII), Since halogen (for example, fluoride) is included, at the time of emergency combustion, it functions also as a scavenger of an activity radical, and an organic substituent also has a screening effect of oxygen in order to generate carbide (char) on a polar material and a separator at the time of combustion. In addition, also when a user charges accidentally, since this isomer has the depressor effect of dendrite generation, as compared

with an additive-free system, safety becomes higher. Since Lynn acts to control chain disassembly of a polymer material which constitutes a cell, self-extinguishing thru/or fire retardancy are revealed effectively.

[0100]In an electrolysis solution containing a supporting electrolyte used as an ester system organic solvent used for the conventional lithium primary cell, and a source of a lithium ion, Although the conductivity of an electrolysis solution may fall when a supporting electrolyte decomposes with temporality and a decomposition product reacts to a little water etc. which exist in an organic solvent, or degradation of a polar material may be produced, If a phosphazene derivative expressed with an isomer expressed with formula (VI) by the conventional electrolysis solution and formula (VII) is added, decomposition of a supporting electrolyte will be controlled and it will contribute to stabilization of an electrolysis solution remarkably. Generally as a supporting electrolyte, LiBF_4 , LiPF_6 , LiCF_3SO_3 , $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, LiCF_3SO_3 with low hydrolysis of the supporting electrolyte itself in which $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ etc. are used, Although $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ and especially $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ are preferred, LiBF_4 and LiPF_6 can also be conveniently used by the above-mentioned operation of this isomer and phosphazene.

[0101]An isomer of a phosphazene derivative which is expressed with formula (VI) and expressed with formula (VII) may make the low-temperature characteristic which was extremely excellent in an electrolysis solution reveal, when added by electrolysis solution.

[0102]As R^7 in formula (VI), R^8 , and R^9 , if it is a substituent or a halogen of monovalence, there will be no restriction in particular and an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. will be mentioned as a substituent of monovalence. As a halogen, halogens, such as fluoride, chlorine, and bromine, are mentioned suitably, for example. Also in these, fluoride, an alkoxy group, etc. are especially preferred the low-temperature characteristic of an electrolysis solution, and in respect of electrochemical stability. An alkoxy group containing fluoride, an alkoxy group, fluoride, etc. are preferred in respect of hypoviscosity-izing of an electrolysis solution. The same kind of substituent may be sufficient as all of $\text{R}^7 - \text{R}^9$, and a substituent of a kind from which some of them differ may be sufficient as them.

[0103]As an alkoxy group, alkoxy substitution alkoxy groups, such as a methoxy group, an ethoxy basis, a propoxy group, a butoxy group, etc. a methoxyethoxy group, a methoxyethoxy ethoxy basis, etc. are mentioned, for example. Also in these, all are preferred for a methoxy group, an ethoxy basis, a methoxyethoxy group, or a methoxyethoxy ethoxy basis as $\text{R}^7 - \text{R}^9$, and it is preferred that a viewpoint of hypoviscosity and high permittivity to all are especially a methoxy group or an ethoxy basis. As an alkyl group, a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, etc. are mentioned. As an acyl group, a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, etc. are mentioned. As an aryl group, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As for a hydrogen element in these substituents, being replaced by halogen is preferred, and fluoride, chlorine, bromine, etc. are suitably mentioned as a halogen.

[0104]In formula (VI), as a divalent connecting group expressed with Y^7 and Y^8 , For example, sulfur, selenium, oxygen, nitrogen besides CH_2 group, boron, Aluminum, a scandium, gallium, yttrium, indium, A lantern, thallium, carbon, silicon, titanium, tin, germanium, A zirconium, lead, Lynn, vanadium, arsenic, niobium,

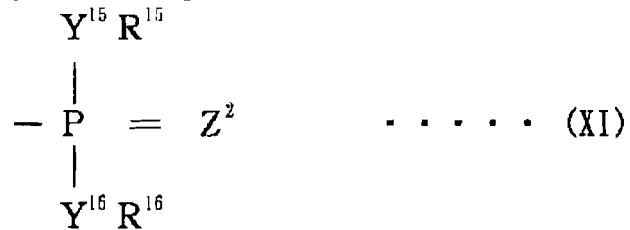
antimony, Tantalum, bismuth, chromium, molybdenum, a tellurium, polonium, tungsten, A divalent connecting group containing at least one sort of an element chosen from a group which a divalent connecting group containing at least one sort of an element chosen from a group which consists of iron, cobalt, and nickel is mentioned, and consists of CH_2 group and oxygen, sulfur, selenium, and nitrogen also in these is preferred. Y^7

and Y^8 may be divalent elements, such as oxygen, sulfur, and selenium, or a single bond. A divalent connecting group which contains an element of sulfur and/or oxygen in a point whose fire retardancy of an electrolysis solution improves, oxygen elements, and especially a sulfur element are preferred, and a divalent connecting group which contains oxygen elements in that it excels in the low-temperature characteristic of an electrolysis solution, and especially oxygen elements are preferred. An identical kind may be sufficient as Y^7 and Y^8 , and a mutually different kind may be sufficient as them.

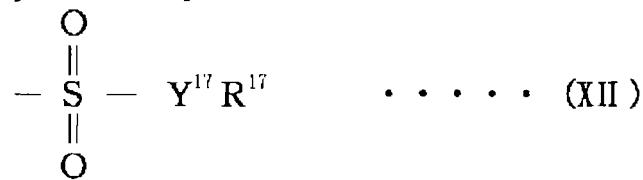
[0105]In formula (VI), as X^2 , A substituent which contains at least one sort of carbon, silicon, nitrogen, Lynn, oxygen, and an element chosen from a group which consists of sulfur from a viewpoint of consideration of hazardous property, environment, etc. is preferred, and a substituent which has the structure expressed with following formula (XI), (XII), or (XIII) is more preferred.

[0106]

[Formula 13]



[Formula 14]



[Formula 15]



[0107]However, in formula (XI), (XII), and (XIII), $\text{R}^{15} - \text{R}^{19}$ express the substituent or halogen of monovalence. $\text{Y}^{15} - \text{Y}^{19}$ express a divalent connecting group, a divalent element, or a single bond, and Z^2 expresses a divalent basis or divalent element.

[0108]In formula (XI), (XII), and (XIII), each substituents or halogens of the same monovalence are mentioned suitably as R^7 in formula (VI) - R^9 described as $\text{R}^{15} - \text{R}^{19}$. A kind from which respectively same kind may be

sufficient and some differ mutually in an identical substituent may be sufficient as these. It may combine with each other and R¹⁵ and R¹⁶ of formula (XI), and R¹⁸ and R¹⁹ of formula (XIII) may form a ring.

[0109]In formula (XI), (XII), and (XIII), as a basis expressed with Y¹⁵ - Y¹⁹, The same divalent connecting group or divalent element is mentioned, and similarly, when it is a divalent connecting group containing an element of sulfur and/or oxygen, oxygen elements, or a sulfur element, especially since the fire retardancy of an electrolysis solution improves, it is as desirable as Y⁷ in formula (I) - Y⁸ described. A divalent connecting group which contains oxygen elements in that it excels in the low-temperature characteristic of an electrolysis solution, and especially oxygen elements are preferred. A kind from which respectively same kind may be sufficient and some differ mutually in an identical substituent may be sufficient as these.

[0110]In formula (XI), they are CH₂ group and CHR (R expresses an alkyl group, an alkoxy group, a phenyl group, etc.) as Z², for example. It is the same as that of the following. Sulfur, selenium, oxygen, boron besides a basis and NR basis, aluminum, A scandium, gallium, yttrium, indium, a lanthanum, thallium, Carbon, silicon, titanium, tin, germanium, a zirconium, lead, Lynn, Vanadium, arsenic, niobium, antimony, tantalum, bismuth, chromium, A divalent basis containing at least one sort of an element chosen from a group which consists of molybdenum, a tellurium, polonium, tungsten, iron, cobalt, and nickel are mentioned, A divalent basis containing at least one sort of an element chosen from a group which consists of oxygen, sulfur, and selenium besides CH₂ group, a CHR basis, and NR basis also in these is preferred. Z² may be divalent elements, such as oxygen, sulfur, and selenium. When it is a divalent basis which contains sulfur and/or elemental selenium especially, a sulfur element, or elemental selenium, since the fire retardancy of an electrolysis solution improves, it is desirable. A divalent basis which contains oxygen elements in that it excels in the low-temperature characteristic of an electrolysis solution, and especially oxygen elements are preferred.

[0111]It is a point which may reveal self-extinguishing thru/or fire retardancy effectively especially as these substituents, and especially a substituent including Lynn which is expressed with formula (XI) is preferred. In formula (XI), especially when Z², Y¹⁵, and Y¹⁶ are oxygen elements, it becomes possible to make the low-temperature characteristic which was extremely excellent in an electrolysis solution reveal. Especially when a substituent is a substituent containing sulfur that it is expressed with formula (XII), it is desirable in respect of formation of small interfacial resistance of an electrolysis solution.

[0112]R⁷ in formula (VI) and (XI) - (XIII) - R⁹, Preparation of an electrolysis solution which has more suitable viscosity, solubility suitable for addition and mixing, the low-temperature characteristic, etc. is attained by choosing suitably R¹⁵ - R¹⁹, Y⁷ - Y⁸, Y¹⁵ - Y¹⁹, and Z². These compounds may be used by an one-sort independent, and may use two or more sorts together.

[0113]An isomer expressed with formula (VI) is an isomer of a phosphazene derivative expressed with formula (VII), For example, it can manufacture by adjusting a degree of vacuum and/or temperature at the time of generating a phosphazene derivative expressed with formula (VII), and content (volume %) in an electrolysis solution of this isomer can be measured with the following measuring method. A peak area of a sample is determined with <<measuring method >> gel permeation chromatography (GPC) or high performance chromatography, It can measure by obtaining a mole ratio by measuring this peak area with area per mol of

said isomer for which it asked beforehand, and also carrying out volume conversion in consideration of specific gravity.

[0114]As a phosphazene derivative expressed with formula (VII), viscosity is comparatively low and what may dissolve a supporting electrolyte good is preferred. As $R^7 - R^9$, $Y^7 - Y^8$, and X^2 of formula (VII), all of that explanation of R^7 of formula (VI) - R^9 , $Y^7 - Y^8$, and X^2 described and same thing are mentioned suitably.

[0115]As the flash point of a phosphazene derivative expressed with formula (VII), although there is no restriction in particular, from points, such as control of ignition, not less than 100 ** is preferred, and not less than 150 ** is more preferred. If a phosphazene derivative has the flash point at not less than 100 **, even if ignition etc. are controlled and ignition etc. arise inside a cell, it will become possible to reduce a danger of igniting and spreading to the electrolysis solution surface.

[0116]It is preferred to have a substituent containing a halogen as molecular structure of a phosphazene derivative expressed with an isomer and formula (VII) which are expressed with formula (VI). As this halogen, fluoride, chlorine, bromine, etc. are preferred and especially fluoride is preferred. If it has a substituent which contains a halogen in molecular structure, it will become possible to make self-extinguishing thru/or fire retardancy reveal at least more effectively of content of these substances with halogen gas derived. In a compound which has a substituent containing a halogen, although generating of halogen radicals may pose a problem, In said isomer and a phosphazene derivative, in order that a phosphorus element in molecular structure may catch halogen radicals and may form stable phosphorus halide, such a problem is not generated.

[0117]As content in an isomer and a phosphazene derivative of a halogen, 2 to 80 % of the weight is preferred, 2 to 60 % of the weight is more preferred, and 2 to 50 % of the weight is still more preferred. Since viscosity will become high if it exceeds 80 % of the weight while an effect that content makes a halogen contain in less than 2 % of the weight may not fully show up, when it adds to an electrolysis solution, the conductivity may fall.

[0118]As a total content with a phosphazene derivative expressed with an isomer expressed with formula (VI) in an electrolysis solution, and formula (VII), By an effect acquired by containing this isomer and this phosphazene derivative. Four kinds of content, the 1st content that can give the "low-temperature characteristic" suitably with an electrolysis solution, the 2nd content that can give "degradation-proof nature" suitably for an electrolysis solution, the 3rd content that can give "self-extinguishing" suitably for an electrolysis solution, and the 4th content that can give "fire retardancy" suitably for an electrolysis solution, are mentioned.

[0119]More than 1 volume % of the 1st content with a phosphazene derivative expressed with an isomer expressed with formula (VI) in an electrolysis solution and formula (VII) from a viewpoint of the "low-temperature characteristic" is preferred, more than its 2 volume % is more preferred, and more than its 5 volume % is still more preferred. Unless content is less than 1 volume %, the low-temperature characteristic of an electrolysis solution is not enough.

[0120]More than 2 volume % of the 2nd content with a phosphazene derivative expressed with an isomer expressed with formula (VI) in an electrolysis solution and formula (VII) from a viewpoint of "degradation-proof nature" is preferred, and its 3 - 75 volume % is more preferred. From a viewpoint that it is highly compatible in degradation-proof nature and the low-temperature characteristic, 5 - 75 volume % is more preferred. If content

is in said numerical value range, it can control degradation suitably.

[0121]More than 20 volume % of the 3rd content with a phosphazene derivative expressed with an isomer expressed with formula (VI) in an electrolysis solution and formula (VII) from a viewpoint of "self-extinguishing" is preferred. Content cannot make sufficient self-extinguishing for an electrolysis solution reveal by less than 20 volume %.

[0122]More than 30 volume % of the 4th content with a phosphazene derivative expressed with an isomer expressed with formula (VI) in an electrolysis solution and formula (VII) from a "fire-resistant" viewpoint is preferred. If content is more than 30 volume %, it will become possible to make sufficient fire retardancy for an electrolysis solution reveal of it.

[0123]From a viewpoint of "self-extinguishing thru/or fire retardancy", as an electrolysis solution, A phosphazene derivative expressed with an isomer and formula (VII) which are formula (VI) and are expressed, A phosphazene derivative expressed with an isomer and formula (VII) which are expressed with formula (VI) when LiBF₄, and gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included,

Especially a case where LiCF₃SO₃, and gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included is preferred. It is not concerned with the above-mentioned statement in these cases, but even if content in an electrolysis solution of an isomer and a phosphazene derivative is little, it has outstanding self-extinguishing thru/or a fire-resistant effect.

[0124]Namely, a phosphazene derivative expressed with an isomer and formula (VII) which are expressed with formula (VI), When LiBF₄, and garnma-butyrolactone and/or propylene carbonate more than 45 volume % are included, As a total content in an electrolysis solution of this isomer and this phosphazene derivative, in order to make self-extinguishing reveal, 1.5 - 10 volume % is preferred, and in order to make fire retardancy reveal, quantity exceeding 10 volume % is preferred. A phosphazene derivative expressed with an isomer and formula (VII) which are expressed with formula (VI), When LiCF₃SO₃, and gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included, As a total content in an electrolysis solution of this isomer and this phosphazene derivative, in order to make self-extinguishing reveal, 2.5 - 15 volume % is preferred, and in order to make fire retardancy reveal, quantity exceeding 15 volume % is preferred.

[0125]As other members used for a lithium primary cell of this invention, a separator made to intervene between positive and negative poles by a role which prevents a short circuit of current by contact of two poles is mentioned in a lithium primary cell. contact of two poles being prevented certainly and as construction material of a separator, A nonwoven fabric made of synthetic resins, such as material which can let pass or contain an electrolysis solution, for example, polytetrafluoroethylene, polypropylene, polyethylene, a cellulose type, polybutylene terephthalate, and polyethylene terephthalate, a thin layered film, etc. are mentioned suitably. Also in these, especially films, such as polypropylene about 20-50 micrometers thick or a microporous film made from polyethylene, a cellulose type, polybutylene terephthalate, and polyethylene terephthalate, are preferred. In this invention, each publicly known member usually used for a cell other than an above-mentioned separator can use it conveniently.

[0126]As a gestalt of a lithium primary cell of this invention explained above, there is no restriction in particular and various publicly known gestalten, such as a coin type, a button type, a paper type, a square shape, or a

cylindrical cell of spiral structure, are mentioned suitably. In a button type case, sheet shaped anode and negative electrode can be produced, and it can produce a lithium primary cell by inserting a separator with this anode and a negative electrode etc. A sheet shaped anode is produced, in the case of spiral structure, a charge collector can be inserted, and it can produce a lithium primary cell by piling up and winding up a negative electrode (sheet shaped) to this etc., for example.

[0127] Since it is preferred that particles of a very detailed metallic oxide are distributed among particles of manganese dioxide as for an anode for lithium primary cells of this invention, a metallic oxide is preferably prepared by a sol gel process. If only it can prepare very detailed particles, the method of preparation in particular is not restricted.

[0128] An anode used for a lithium primary cell of this invention can be manufactured according to the following 1st thru/or the 4th process. In the 1st process, an alkoxide of at least one sort of metal chosen from a group which consists of manganese dioxide, titanium and aluminum, zinc, chromium, lithium, nickel, copper, and iron into an organic solvent is added, it mixes, and mixed liquor is prepared. As an organic solvent, low-boiling point ketone, such as low-boiling point alcohol, such as methanol and ethanol, or acetone, is preferred, and especially ethanol is preferred. As an alkoxy group [in / on the other hand / a metal alkoxide], an isopropoxy group from a soluble viewpoint of a metal alkoxide over an organic solvent, n-propoxy group, etc. are preferred.

[0129] In the 2nd process, water is added to mixed liquor prepared at the 1st process, and a hydrolysis reaction of said metal alkoxide generates metal hydroxide corresponding to this metal alkoxide. As for the 2nd process, it is preferred to carry out ice-cooling.

[0130] Next, by heating and drying liquid containing metal hydroxide at the 3rd process, metal hydroxide is used as a metallic oxide, removing a solvent, and powder for anodes which distributed this metallic oxide among manganese dioxide particles is manufactured. As for heating and desiccation, in order to perform removal and drying of a solvent thoroughly, it is preferred to carry out time sufficient at temperature of 120-300 **.

[0131] Next, powder for anodes obtained at the 3rd process is fabricated in predetermined shape at the 4th process, and an anode for lithium primary cells is obtained at it. A forming process will not be limited especially if an anode of intensity of a grade which is not damaged by a manufacturing process of a lithium primary cell can be fabricated, but a publicly known method can be conventionally used for it. For example, it can carry out also by piercing said powder for anodes with a clicking machine with a mold corresponding to shape of an anode of the target lithium primary cell. After mixing and kneading additive agents, such as the above-mentioned conducting material and a binder, making them into paste state and carrying out hot air drying (100-120 **) to powder for anodes before shaping, it may pierce with a clicking machine.

[0132]

[Example] Although an example is given to below and this invention is explained to it in more detail, this invention does not have the range limited by these examples.

[0133] (Example 1) The anode for lithium primary cells was produced by the following method. Into ethanol 10mL, 0.07 g (0.25mmol) titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) is added, and it agitated for 30 minutes and was made to dissolve under the atmosphere. Next, agitating, 1 g of manganese dioxide (Mitsui Mining

EMD) was added, and the generated ethanol solution was distributed. Next, ice-cooling these dispersion liquid, water 0.5mL (27mmol) was added to this, and, thereby, titanium isopropoxide was used as titarium hydroxide ($Ti(OH)_4$). Next, stoving of the mixed liquor containing the generated titanium hydroxide was carried out at 80 **, further, by drying at 300 ** for 1 hour, titanium hydroxide was used as titanium oxide and the powder in which this titanium oxide was distributed among manganese dioxide particles was obtained. Thus, the obtained powder was taught to the oven of the glass tube, and it dried at 100 ** for 1 hour, and was made the powder for anodes. The mass of titanium oxide in the powder for anodes was 2% to the mass of manganese dioxide.

[0134]8:1:1 mixes and kneads comparatively (mass ratio) this powder for anodes, acetylene black, and polytetrafluoroethylene (PTFE), After carrying out coating of this kneaded material with a doctor blade, the anode for lithium primary cells was produced by starting what was obtained by carrying out hot air drying (100-120 **) with phi16-mm clicking machine. The mass of an anode is 19 mg. The lithium primary cell was produced as follows using this anode.

[0135]What pierced lithium foil (0.5 mm in thickness) to phi16mm was used for the negative electrode, and nickel foil was used for the charge collector. An electrolysis solution is the phosphazene derivative A (in said formula (IV), n is 3.).

The annular phosphazene derivative compound whose two are an ethoxy basis and whose four are fluoride among six R, and viscosity:1.2 mPa·s (1.2 cP) 10 volume % at 25 **, It prepared by dissolving $LiBF_4$ (lithium salt) in a mixed solution with gamma-butyrolactone (GBL) 90 volume % by the concentration of 0.75 mol/L (M).

[0136]Used the cellulose separator (TF4030 by a Japanese advanced paper-making business company) as a separator, the above-mentioned positive and negative poles were made to sit opposite to each other via this, the above-mentioned electrolysis solution was poured in and obturated, and the CR2016 type lithium primary cell was produced.

[0137]It asked for the battery characteristic of the lithium primary cell of this example with the following test method, and it was compared with the general-purpose lithium primary cell as a conventional example. A general-purpose lithium primary cell does not distribute titanium oxide among manganese dioxide particles, and the mass of an anode is 19 mg.

It has the same structure as the lithium primary cell of Example 1 except having used the electrolysis solution which was made to dissolve $LiBF_4$ (lithium salt) in gamma-butyrolactone (GBL) by the concentration of 0.75 mol/L (M), and was prepared.

[0138]These cells were discharged to 1.5V (lower limit voltage) by 1 mA (0.2C) of constant current under the 25 ** atmosphere, and the ordinary temperature discharge curve shown in drawing 1 was obtained. A solid line shows the discharge curve of Example 1 among a figure, and a dotted line shows the discharge curve of a conventional example.

[0139]When service capacity was calculated from the discharge curve of drawing 1, the service capacity of Example 1 was 298 mAh/g, and they were 235 mAh/g in the conventional example.

[0140]When it integrated with the charging-time-value-voltage curve and asked for the energy density based on the discharge curve of drawing 1, the energy densities of Example 1 were 726 Wh/kg, and they were 583 Wh/kg in the conventional example.

[0141]The limiting oxygen index of the electrolysis solution of Example 1 and a conventional example was measured according to JIS K 7201. As a result, in the electrolysis solution of Example 1, the limiting oxygen index was 25.1 volume %, and it was 17.1 volume % in the electrolysis solution of the conventional example.

[0142](Examples 2-3 and comparative examples 1-2) Except changing the quantity of the titanium oxide distributed among manganese dioxide particles like the Table 1 statement, the powder for anodes was prepared like Example 1, and the lithium primary cell was produced. To the obtained lithium primary cell, measurement of service capacity and an energy density is performed like Example 1, and the result is shown in Table 1.

[0143]

[Table 1]

	単位	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
酸化チタンの量	質量%	2	0.5	4	0.3	5
放電容量	mAh/g	298	290	288	240	260
エネルギー密度	Wh/kg	726	719	704	619	652

[0144](Example 4) Except having distributed the zinc oxide among the particles of manganese dioxide instead of titanium oxide (the mass of the zinc oxide to the mass of manganese dioxide is 2%), the lithium primary cell was produced like Example 1, and service capacity and an energy density were measured similarly. As a result, service capacity was 295 mAh/g and the energy densities were 720 Wh/kg.

[0145](Example 5) It is the phosphazene derivative B (in said formula (IV)) instead of the phosphazene derivative A. The annular phosphazene derivative compound whose n is 3 and whose five one is a methoxy group and are fluoride among six R, Viscosity at 25 **: Except having used 1.8 mPa·s (1.8 cP), the electrolysis solution was prepared like Example 1, the lithium primary cell was produced, and service capacity and an energy density were measured similarly. As a result, service capacity was 297 mAh/g and the energy densities were 725 Wh/kg. When the limiting oxygen index of the electrolysis solution was measured like Example 1, the limiting oxygen index was 25.0 volume %.

[0146](Example 6) It is the phosphazene derivative C (in said formula (IV)) instead of the phosphazene derivative A. The annular phosphazene derivative compound whose n is 4 and whose seven one is an ethoxy basis and are fluoride among eight R, Viscosity at 25 **: Except having used 1.3 mPa·s (1.3 cP), the electrolysis solution was prepared like Example 1, the lithium primary cell was produced, and service capacity and an energy density were measured similarly. As a result, service capacity was 295 mAh/g and the energy densities were 720 Wh/kg. When the limiting oxygen index of the electrolysis solution was measured like Example 1, the limiting oxygen index was 25.8 volume %.

[0147]By distributing titanium oxide among manganese dioxide particles, adding a phosphazene derivative,

and preparing an electrolysis solution from these results, shows that service capacity and an energy density improve remarkably, and the limiting oxygen index of an electrolysis solution rises and safety improves greatly.

[0148]

[Effect of the Invention]A lithium primary cell consists of this inventions using the anode which consists of powder which distributed the specific metallic oxide, and the electrolysis solution which added the isomer of the phosphazene derivative and/or the phosphazene derivative among the particles of manganese dioxide. Therefore, since service capacity and the energy density are high, a lithium primary cell with high safety can be provided long lasting by high power.

[Translation done.]